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REPORT NO. 0235-01-23 (QUARTERLY)
PERIOD COVERED: 1 APRIL – 30 JUNE 1965

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

A REPORT TO

OFFICE OF NAVAL RESEARCH

AND

ADVANCED RESEARCH PROJECTS AGENCY

CONTRACT Nonr 2655(00)
ARPA ORDER NO. 170, AMENDMENT NO. 7
PROJECT CODE 4910

AUGUST 1965

COPY NO. [redacted]

CHEMICAL PRODUCTS DIVISION
AEROJET-GENERAL CORPORATION
AZUSA, CALIFORNIA

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August 1965

Report No. 0235-01-23
(Quarterly)

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

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A Report to

OFFICE OF NAVAL RESEARCH
and
ADVANCED RESEARCH PROJECTS AGENCY

Contract NOnr 2655(00)
ARPA Order No. 170, Amendment No. 7
Project Code 4910

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Von Karman Center

AEROJET-GENERAL CORPORATION

A Subsidiary of The General Tire & Rubber Company

Report No. 0235-01-23

ABSTRACT

The nitrosation of the salt of 1,1-dinitropropane gave 1,1-dinitro-1-nitrosopropane, an unstable compound identified as its Diels-Alders adduct with 2,3-dimethylbutadiene. The reaction of 1,1-dinitro-1-nitrosopropane with difluoramine and fuming sulfuric acid gave 1,1-dinitropropane, and no C-NF_2 compound. The reaction of α,α-dibromo-α-difluoraminotoluene with liquid ammonia gave α-bromo-α-fluoriminotoluene. The reaction of cyclopentyldifluoramine with sulfuric acid gave the imonium ion resulting from fluoride loss and ring expansion.

The fluorination of 1-carboalkoxyguanidines, $NH_2C(=NH)NHCO_2R$, where R = CH_3, C_2H_5, i-C_3H_7, and n-C_4H_9, gave the corresponding tetrafluoro derivatives, $NF_2C(=NF)NFCO_2R$, coded as CPFG (carboalkoxyperfluoroguanidine). The fluorination of 1,3-dicarboalkoxyguanidines gave the corresponding trifluoro derivatives, $NH=C(NFCO_2R)_2$, coded as DCPFG (1,3-dicarboalkoxyperfluoroguanidine), as well as smaller amounts of CPFG. Attempts to add methanol or ethanol to the fluorimino group of either CPFG or DCPFG were unsuccessful. Reactions of DCPFG with concentrated mineral acids were investigated briefly.

Fluorammonium perchlorate was found to be stable for at least 3 months at room temperature in nickel containers. The material is relatively insensitive to electrostatic shock. The reaction of fluorammonium methanesulfonate with water gave nitrogen, ammonia, and hydrazine. The reaction with acetic anhydride gave N-methylacetamide.

Report No. 0235-01-23

CONTRACT FULFILLMENT STATEMENT

This is the twenty-third in a series of quarterly technical reports submitted in partial fulfillment of the contract. It covers the period of 1 April through 30 June 1965.

AEROJET-GENERAL CORPORATION

H. W. Thomas for
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L. R. Rapp, Manager
Chemical and Structural Products Division

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I. INTRODUCTION

The objective of this program is to develop new methods of preparing high-energy materials for military application. During the period covered in this report, research was continued on the reactions of difluoramine, on liquid-phase fluorination of nitrogenous compounds, and on the preparation of fluorammonium perchlorate.

II. TECHNICAL DISCUSSION

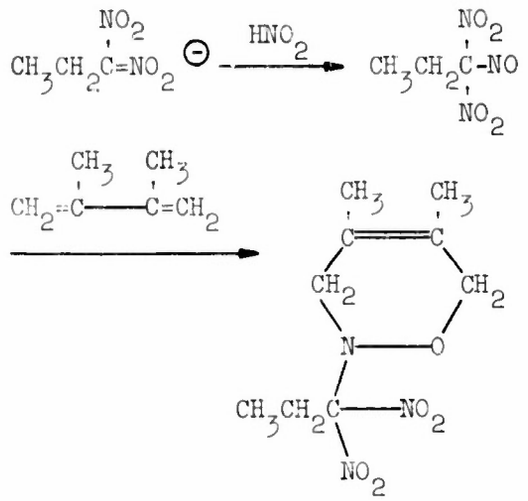
A. REACTIONS OF DIFLUORAMINE (K. Baum)

1. Discussion

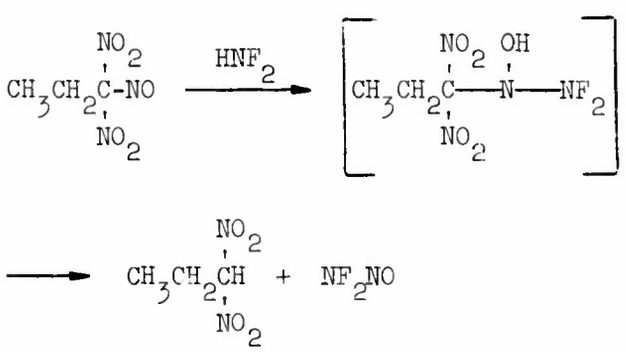
1-Halo-1-nitro-1-nitrosoalkanes have been shown to undergo replacement of nitro and nitroso groups by difluoramino groups in the reaction with difluoramine in sulfuric acid.* During the current report period, efforts were made to extend this reaction to 1,1-dinitro-1-nitrosoalkanes, a previously unreported class of compounds.

The nitrosation of the sodium salt of 1,1-dinitropropane at 0°C in aqueous solution resulted in the precipitation of a dark-blue oil. The material was too unstable for purification by distillation, however; a sample kept at room temperature decomposed within about 30 minutes. The structure of the product was demonstrated by adding 2,3-dimethyl-1,3-butadiene to a freshly prepared sample. The crystalline Diels-Alder adduct, isolated in 71-5% yield, was characterized by elemental analysis.

*Aerojet-General Report 2945, October 1964 (Confidential).



The reaction of a freshly prepared sample of 1,1-dinitro-1-nitrosopropane with difluoramine was carried out using 20% fuming sulfuric acid as the catalyst. When the reaction mixture was quenched, extracted, and distilled, a 45% yield of 1,1-dinitropropane was obtained. No other product was isolated. Apparently, the inductive effect of the two nitro groups is sufficient to prevent the formation of a carbonium ion, so that the nitroso compound acts as a nitrosating agent toward difluoramine. In addition compound may be an intermediate.



This reaction course has been reported for the reaction of 1-nitro-1-nitrosocyclohexane, in addition to the alternative mode of cleavage leading to the gem-difluoramine.*

*Aerojet-General Report 0235-01-20, July 1964, p. 2 (Confidential).

Some reactions of model α-halodifluoramines have been presented in the preceding report.* In a continuation of this work, the reaction of α,α-dibromo-α-difluoraminotoluene with liquid ammonia was examined. A 30% yield of α-bromo-α-fluoriminotoluene was isolated. This compound was previously obtained** from the reaction of sodium 2-propanenitronate with α,α-dibromo-α-difluoramino-toluene, but the elemental analysis and spectra showed that the material was not pure. The present product, however, was analytically pure.

$$C_6H_5CBr_2NF_2 \xrightarrow{NH_3} C_6H_5\underset{Br}{C}=NF$$

Since secondary α-halo-nitro compounds have been shown to react readily with difluoramine in sulfuric acid to give gem-difluoramines, work was begun on the preparation of a high-energy polymer utilizing this reaction. The polymer of 1-chloro-1-nitroethylene, reported by Wilkendorf and Trenel,*** could give an adduct containing one NF_2 group per carbon atom.

The synthesis of 1-chloro-1-nitroethylene by the reported method, the reaction of chloronitroethanol with phosphorous pentoxide gave a 68% of the olefin. The structure was confirmed by elemental analysis and infrared (see Figure 1) and NMR (Figure 2) spectra. This olefin polymerized rapidly on contact with aqueous sodium bicarbonate solution. The polymer will be reacted with difluoramine in sulfuric acid.

Some further work has also been carried out on the reaction of alkyldifluoramines with sulfuric acid. Cyclopentyldifluoramine reacted readily with concentrated sulfuric acid at 0°C. The proton (see Figure 3) and fluorine (Figure 4) NMR spectra of the sulfuric acid solution are consistent with the ring-expanded fluorimonium ion:

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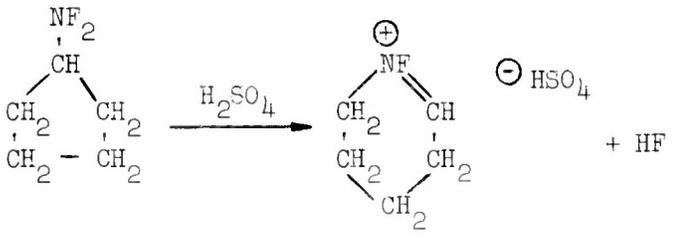
* Aerojet-General Report 0235-01-22, May 1965, p. 5 (Confidential).

** Ibid.

*** R. Wilkendorf and M. Trenel, Ber., 57, 308 (1924).



In the proton spectrum, the pair of unresolved triplets at 8.83 ppm is assignable to the =CH proton, with coupling constants of 25.2 cps to the fluorine and 2-3 cps to the adjacent methylene. The doublet at 4.28 ppm (2.8 cps splitting) is assigned to the methylene group adjacent to the NF, and the multiplet at 3.13 ppm, to the methylene adjacent to the =CH-. The multiplets at 137 cps and 116 cps are attributed to the remaining methylene groups. The fluorine spectrum contains an HF signal at -116.57 ppm and a broadened NF doublet at -157.53 ppm with coupling of 24.1 cps to the =CH- proton.

It is of interest to compare these spectra with those of the next higher homologue, derived from cyclohexyldifluoramine.* The triplet splitting of the latter was approximately double that of the cyclopentyldifluoramine product. The coupling constants of the vinyl hydrogens of cycloheptene and cyclohexene to the adjacent methylenes are in the same ratio.** In the cyclohexyldifluoramine product, the coupling constant of fluorine to the adjacent methylene is 12-13 cps, while that of the cyclopentyldifluoramine product, observable only in the proton spectrum, is 2.8 cps. The large changes of the coupling constants with ring size are attributed to changes in the dihedral angles.

2. Experimental

a. 1,1-Dinitro-1-nitrosopropane

To a solution of 10.0 g (0.075 moles) of 1,1-dinitropropane and 3.0 g (0.075 moles) of sodium hydroxide in 50 ml of water, 5.15 g (0.075 moles) of sodium nitrite was added. The resulting solution was cooled with a -80° bath until it was partially frozen, and 10% aqueous sulfuric acid was

*Aerojet-General Report 2381, October 1962, p. 11 (Confidential).

**G. V. Smith and H. Kriloff, J. Am. Chem. Soc., 85, 2016 (1963); K. B. Wiberg and B. J. Nist, J. Am. Chem. Soc., 83, 1226 (1961).

added dropwise, with swirling. A dark-blue oil precipitated, and acid was added until the precipitation ceased. The reaction mixture was cooled intermittently with a -80° bath in order to keep it partially frozen. The product was extracted with 15 g of methylene chloride to give 22 g of solution (7 g of product).

b. Reaction of 1,1-Dinitro-1-nitrosopropane with Difluoramine

The freshly prepared solution of 1,1-dinitro-1-nitrosopropane was added, with stirring, to a refluxing mixture of 27 g of difluoramine and 6 ml of 20% fuming sulfuric acid. The blue color of the nitroso compound was bleached on contact with the reagent. After 2 hours, the mixture was drained onto 200 ml of ice, and the product was extracted with two 25-ml portions of methylene chloride. The methylene chloride solution was dried over sodium sulfate and distilled to yield 4.51 g (45% recovery) of 1,1-dinitropropane, bp 66°/3 mm. The infrared spectrum of this material was identical to that of an authentic sample.

c. 2,3-Dimethylbutadiene Adduct of 1,1-Dinitro-1-nitrosopropane

To a solution of 1.34 g (0.001 mole) of 1,1-dinitropropane, 0.4 g (0.01 mole) of sodium hydroxide, in 8 ml of water, 0.69 g (0.01 mole) of sodium nitrite was added. The solution was frozen, partially, and 10% aqueous sulfuric acid was added dropwise with swirling until precipitation of blue oil ceased. To this mixture, 2.5 g (0.0305 moles) of 2,3-dimethyl-1,3-butadiene was added, and the reaction was maintained at 0° with agitation for several minutes, until the blue color disappeared. The product was extracted with 50 ml of methylene chloride, and the resulting solution was dried over sodium sulfate and stripped of solvent. A viscous liquid remained, which crystallized when 10 ml of pentane was added. The crude adduct (1.75 g, 0.00715 mole, 71.5% yield) was a slightly yellow solid, mp 105-107°. An analytical sample, obtained by recrystallizing the crude material from chloroform-carbon tetrachloride, consisted of white needles, mp 110°.

Anal. Calc'd for $C_9H_{15}N_3O_5$: C, 44.2; H, 6.13; N, 17.15.
Found: C, 44.8; H, 6.48; N, 17.9.

d. Reaction of α,α-Dibromo-α-difluoraminotoluene with Ammonia

Liquid ammonia (10 ml) was condensed into a three-necked 50-ml flask fitted with a -80° condenser, a magnetic stirrer, and a dropping funnel containing 2.45 g (0.00815 moles) of α,α-dibromo-α-difluoraminotoluene. The α,α-dibromo-α-difluoraminotoluene was added dropwise, with stirring, and stirring was continued for 1 hour after the addition was completed. Ether (15 ml) was added and the excess ammonia was allowed to escape. The ether layer was decanted from a white solid which precipitated. Removal of the solvent and vacuum distillation of the residue gave 0.50 g (0.0025 moles, 30.4% yield) of α-bromo-α-fluoriminotoluene, bp 29°/0.5 mm.

Anal. Calc'd for C_7H_5NFBr: C, 41.6; H, 2.48; N, 6.93; F, 9.40.
Found: C, 41.4; H, 2.56; N, 6.77; F, 9.54.

The infrared spectrum of this material was virtually identical to that reported previously* for an impure sample, except for small peaks at 6.2, 7.55 and 15.0 μ which disappeared. The F^{19} NMR spectrum contained only a singlet at -64.18 ppm ($CFCl_3$ standard). The proton NMR spectrum was identical to that of the previous sample** except for the absence of the peaks at 4.09 and 1.68 ppm.

e. 1-Chloro-1-nitroethylene

Phosphorous pentoxide (7.2 g) was placed in a 50-ml three-necked flask fitted with a dropping funnel and a dry-ice-cooled vacuum receiver. The system was evacuated to 20 mm Hg, and 2-chloro-2-nitroethanol*** (6.7 g, 0.048 moles) was added slowly from the dropping funnel. The mixture was then heated to 170°C, and the pressure was reduced gradually to 0.1 mm. The material that collected in the receiver was distilled through a Holzmann column to yield 3.5 g (0.0325 moles, 68% yield) of 1-chloro-1-nitroethylene, pb 43°/50 mm, an extremely strong lachrymator.

Anal. Calc'd for $C_2H_2ClNO_2$: C, 22.4; H, 1.86; N, 13.0.
Found: C, 22.0; H, 2.04; N, 13.2.

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*
**Aerojet-General Report 0235-01-22, May 1965, Figure 6 (Confidential).
***Ibid., Figure 7.
R. Wilkendorf, Ber., 56, 611 (1923).

B. DIRECT FLUORINATION (V. Grakauskas)

1. Discussion

1-Carboalkoxyguanidines and 1,3-dicarboalkoxyguanidines might be expected to undergo direct fluorination to give the corresponding trifluoro- and tetrafluoroguanidine derivatives and PFG:

$$NH_2C(=NH)NHCO_2R + F_2 \longrightarrow NH_2C(=NF)NHCO_2R \xrightarrow{F_2} \longrightarrow NF_2C(=NF)NFCO_2R \xrightarrow{F_2} PFG$$

$$NH=C(NHCO_2R)_2 + F_2 \longrightarrow NF=C(NHCO_2R)_2 \xrightarrow{F_2} NF=C(NFCO_2R)_2 \xrightarrow{F_2} PFG$$

These substituted perfluoroguanidines might undergo addition reactions analogous to those reported for PFG.

1-Carboalkoxyguanidines, $NH_2D(=NH)NHCO_2R$, where R = CH_3, C_2H_5, i-C_3H_7 and n-C_4H_9, were synthesized in 40-70% yields by reacting aqueous guanidine with molar amounts of the corresponding alkyl chloroformates in the presence of alkali. The infrared spectrum of 1-carbo-n-butoxyguanidine, representative for this series of compounds, is shown in Figure 5. Small amounts of the corresponding 1,3-dicarboalkoxyguanidines (5-15%) were also produced in the above reactions. When the molar ratio of alkyl chloroformates to guanidine was increased to 2:1, 15-25% yields of 1,3-dicarboalkoxyguanidines were obtained. Higher yields of these difunctional derivatives were obtained when the reaction was conducted in alcoholic solution. The infrared spectrum of 1,3-dicarbo-n-butoxyguanidine (Figure 6) is representative for this series of compounds.

The fluorinations of 1-carboalkoxyguanidines were carried out in acetonitrile suspension; the reactions were sluggish and were accompanied by localized firings in the reactor. The reaction was stopped at a 4:1 molar ratio of fluorine to substrate. Four 1-carboalkoxyguanidines, $NH_2C(=NH)NHCO_2R$, where R is CH_3, C_2H_5, i-C_3H_7, and n-C_4H_9, were fluorinated in this manner, and in all cases the main reaction product was identified as the corresponding 1-carboalkoxyperfluoroguanidine:

$$NH_2C(=NH)NHCO_2R + 4\ F_2 \xrightarrow{(CH_3CN)} NF_2C(=NF)NFCO_2R$$

Analytical samples were obtained by gas chromatography. The structures of the 1-carboalkoxyperfluoroguanidines were confirmed by infrared and NMR spectra (Figures 7-18).

To simplify reporting, these structures will be abbreviated as C_nPFG, the subscript indicating the number of carbon atoms in the alkyl group. Thus, C_2PFG designates carboethoxyperfluoroguanidine, and $C_{3i}PFG$, designates carboisopropoxyperfluoroguanidine.

The fluorination of 1,3-dicarboethoxy- and 1,3-dicarboisopropoxyguanidine proceeded more smoothly. When a 3:1 molar ratio of fluorine to substrate was used, the corresponding 1,3-dicarboalkoxyperfluoroguanidines were obtained in 40-50% yields:

$$NH = C(NHCO_2R)_2 + 3\ F_2 \xrightarrow{(CH_3CN)} NF = C(NFCO_2R)_2$$

The two compounds were identified on the basis of their elemental analyses, their infrared spectra (see Figures 19 and 20), and their NMR spectra (Figures 21-24). The 1,3-dicarboalkoxyperfluoroguanidines, coded DC_nPFG, were found to be quite impact-sensitive. For $DC_{3i}PFG$ and DC_4PFG, the 50% firing levels, using an Olin Mathieson tester with a 2-kg weight, were determined to be 3 and 4.5 cm, respectively.

In addition to DCPFG, small amounts (ca. 10-15% yield) of the corresponding CPFG's were also isolated in the above fluorinations indicating displacement of a carboalkoxy group.

$$NF{=}C(NFCO_2R)_2 + F_2 \longrightarrow NF_2C(=NF)NFCO_2R + CO_2 + ROH$$

The CPFG's and DCPFG's were storable without noticeable decomposition at room temperature for at least several weeks. Differential thermal analyses of $C_{4n}PFG$ (see Figure 25) and of $DC_{3i}PFG$ (Figure 26) illustrate the thermal stability of these compounds.

Some preliminary experiments were conducted in order to assess the reactivity of these compounds. In one experiment, an acetonitrile solution of DC_2PFG and methanol containing a catalytic amount of urea was allowed to stand

at room temperature for 24 hours. The NMR spectrum of the reaction mixture indicated no reaction. When an aliquot of the solution was heated at 60-65° for 3 hours, NMR analysis again indicated no reaction. Further attempts to add alcohols to these compounds are in progress.

One attempt was made to determine if a DCPFG reacts with nitric acid. By analogy to the reaction of alkyl N-fluoro-N-alkylcarbamates with 100% nitric acid, 1,3-dinitroperfluoroguanidine, might be formed.*

$$RNFCO_2R' + HNO_3 \longrightarrow RNFNO_2 + CO_2 + R'ONO_2$$

$DC_{3i}PFG$ dissolved without apparent reaction in cold (-10°C) 100% nitric acid. Gas evolution, accompanied by a mild exotherm, began when the reaction mixture was allowed to warm to 20-25°C. When the reaction mixture was quenched with ice water, after 1 hour, only starting material (ca. 30% recovery) was isolated.

DCPFG appeared to be a suitable starting material for the preparation of fluorammonium salts.

$$NF=C(NFCO_2R)_2 + 3\ HX + 4\ H_2O \longrightarrow 3\ NH_3F^+X^- + 3\ CO_2 + 2\ ROH$$

The reaction between $DC_{3i}PFG$ and concentrated sulfuric acid at room temperature gave instantaneous gas evolution. However, the NMR spectrum of the reaction mixture showed no fluorammonium salt.

2. Experimental

a. 1-Carbosiopropoxyguanidine

To a solution of 528 g (8.0 moles) of 85% potassium hydroxide in 1500 ml of water was added with stirring at 15°C, 360 g (2.0 moles; 4.0 equivalents) of guanidine carbonate. The reaction mixture was cooled to 0-2°C and to it was added dropwise over a period of 30 minutes, 491 g (4.0 moles) of isopropyl chloroformate. The reaction mixture was allowed to warm to 14-16°C, at which temperature a mildly exothermic reaction began, and occasional cooling was applied to keep the reaction temperature at 15-20°C. After 45 min the reaction was complete; the reaction mixture was cooled to 0-5°C and the product was

*Aerojet-General Report No. 2381 (Annual Summary), October 1962, p. 39 (Confidential).

collected by filtration. The crude material was crystallized from 650 ml of water to give 180 g of 1-carboisopropoxyguanidine, mp 143-5°C (see Table 1 for elemental analysis).

Water insoluble portion of the product, 60 g, was recrystallized from 200 ml of methanol to give 45 g of 1,3-dicarboisopropoxyguanidine, mp 170°C (see Table 2 for elemental analysis).

b. 1,3-Dicarboethoxyguanidine

To 648 g of 25% methanolic sodium methoxide (3.0 moles of $NaOCH_3$) was added at 15°C with stirring, 95.5 g (1.0 mole) of guanidine hydrochloride. The resulting mixture was stirred vigorously for 30 min and then cooled to 10-12°C. To the cold mixture was added dropwise 217 g (2.0 moles) of ethyl chloroformate over a period of 45 min. The reaction was exothermic and external cooling was applied during this addition. At the end of the run, the reaction mixture was filtered to remove sodium chloride. The filtrate was evaporated to dryness and the residual solid recrystallized from methanol to give 180 g of 1,3-dicarboethoxyguanidine, mp 160-162°C.

c. 1-Carbo-n-butoxyperfluoroguanidine (C_{4n}PFG)

A solution (partial suspension) of 63.6 g (0.4 mole) of 1-carbo-n-butoxyguanidine in 750 ml of acetonitrile was fluorinated at 0 to 5°C until 1.6 moles of fluorine was consumed. The reaction was accompanied by frequent localized firings in the reactor and the reactor contents darkened gradually. The fluorination mixture was washed with 3 liters of ice water, the organic layer was separated, and the material was dissolved in 400 g of methylene chloride. The methylene chloride solution was dried, filtered, and a 25% aliquot of the filtrate was worked up to give 1.5 g of a pale-yellow liquid, bp 70°C/40 mm. Gas chromatographic analysis indicated that this material contained 70-75% of the desired product. An analytical sample was obtained by gas chromatography. (See Table 3 for the elemental analysis and Figure 16 for its infrared spectrum.)

The 60-mc proton (Figure 17) and 56.4-mc fluorine (Figure 18) NMR spectra were obtained using a $CDCl_3$ solution in a Varian microcell. TMS and $CFCl_3$ served as internal references. The assignments are as follows:

H'. The broadened triplet at 4.42 ppm is assigned to the $-CO_2\underline{CH}_2CH_2-$ methylene group. The irregular triplet at 0.97 ppm is assigned to the $-CH_2\underline{CH}_3$ methyl group. The complex multiplet with maximum intensity at 94 cps is assigned to the "internal" methylene groups, $-CH_2\underline{CH}_2\underline{CH}_2CH_3$.

F^{19}. The signals at -45.4 and -42.4 ppm are assigned to syn and anti difluoramino groups. The signals at -32.8 and -25.0 ppm are assigned to syn and anti fluorimino fluorines. The signals at +44.1 and +51.5 ppm are assigned to syn and anti-NFCOO-fluorines.

The proton and fluorine spectra are consistent with the C_{4n}PFG structure.

d. 1-Carboisopropoxyperfluoroguanidine (C_{3i}PFG)

1-Carboisopropoxyperfluoroguanidine was synthesized and isolated following the general procedure described above. The analytical sample was obtained by gas chromatography (see Table 3 for its analysis and Figure 13 for its infrared spectrum).

The 60-mc proton (see Figure 14) and 56.4-mc fluorine (Figure 15) NMR spectra were obtained using methylene chloride solution with TMS and $CFCl_3$ added as internal references. The assignments are as follows:

H'. The doublet at 1.39 ppm is assigned to the isopropyl methyl groups, $-CH(\underline{CH}_3)_2$. The septet (outer members not visible) at 5.21 ppm is assigned to the isopropyl $-\underline{CH}(CH_2)_3$ proton. This multiplet is overlapped by an intense solvent signal. Other weak signals indicate the presence of an impurity.

F^{19}. The signals at -45.52 and -42.68 are assigned to the syn- and anti-difluoramino groups. The signals at -31.6 and -24.24 ppm are assigned to syn- and anti-fluorimino groups. The signals at +44.69 and +52.26 ppm are assigned to syn- and anti- $-\underline{NF}CO$-fluorines. These signals show evidence of unresolved fine structure, but the signal-to-noise ratio was too low to allow splittings to be obtained.

The proton and fluorine spectra are consistent with C_{3i}PFG structure.

e. 1-Carboethoxyperfluoroguanidine (C_2PFG)

1-Carboethoxyperfluoroguanidine was synthesized and isolated following the procedure used for the preparation of C_4PFG (c). An analytical sample was obtained by gas chromatography; see Table 3 for its elemental analysis and Figure 10 for its infrared spectrum.

The 60-mc proton (Figure 11) and 56.4-mc fluorine (Figure 12) NMR spectra were obtained using a $CDCl_3$ solution with TMS and $CFCl_3$ added as internal references. The assignments are as follows:

H'. The quartet at 4.48 ppm and the triplet at 1.41 ppm are assigned to the carboethoxy ethyl group.

F^{19}. The signals at -45.4 and -42.4 ppm are assigned to syn- and anti-difluoramino groups. The signals at -32.0 and -25.0 ppm are assigned to syn- and anti-fluorimino fluorines. The signals at +44.1 and +51.4 ppm are assigned to syn- and anti- -NFCO-fluorines. These signals show evidence of unresolved fine structure.

The proton and fluorine spectra are consistent with C_2PFG structure.

f. 1-Carbomethoxyperfluoroguanidine (C_1PFG)

1-Carbomethoxyperfluoroguanidine was synthesized following the procedure described above (c). Elemental analysis on the compound was not obtained, but its structure was established on the basis of its infrared spectrum (see Figure 7), and NMR spectra (see below).

The 60-mc proton (see Figure 8) and 56.4-mc fluorine (Figure 9) NMR spectra were obtained in carbon tetrachloride solution using TMS and $CFCl_3$ as internal references. The assignments are as follows:

H'. The intense singlet at 4.05 ppm is assigned to the carbomethoxy methyl group. A weak singlet to higher field is apparently due to an impurity.

F^{19}. The fluorine spectrum is complicated by the existence of geometrical isomers involving the fluorimino double bond. The signals at -45.06 and -42.04 ppm are assigned to syn- and

anti-difluoramino groups. The signals at -32.72 and -24.99 ppm are assigned to the syn- and anti-fluorimino fluorines. A weak -23.64 ppm signal is apparently caused by an impurity. The signals at +43.94 and +51.02 ppm are assigned to syn- and anti--NFCO- fluorines. They have the form of poorly resolved quartets with splittings of approximately 6 and 9 cps, respectively. Two relatively weak signals to higher field are further evidence for the presence of an impurity.

g. 1,3-Dicarboethoxyperfluoroguanidine (DC_2PFG)

A suspension of 20.3 g (0.1 mole) of 1,3-dicarboethoxyguanidine in 300 ml of acetonitrile was fluorinated at 0°C until 0.3 moles of fluorine was consumed (1.5 hours). The fluorination mixture was washed with 700 ml of ice water and phases were separated. The organic product 23 g, was dissolved in 130 ml of methylene chloride; the solution was dried and filtered. A 50% aliquot of the filtrate was worked up to give 4.5 g of a pale-yellow liquid, bp 72°C/0.1 mm.

Anal. Calc'd for $C_7H_{10}N_3F_3O_4$: C, 32.69; H, 3.92; N, 16.34; F, 22.17.
Found: C, 32.6; H, 4.1; N, 16.4; F, 21.9.

The infrared spectrum of DC_2PFG is shown in Figure 19. Impact sensitivity of DC_2PFG, obtained on Olin Mathieson Drop Weight Tester using 2 kg weight, is as follows: 0% firing at 4 cm; 50% firing at 4.5 cm; and 100% firing at 5.0 cm.

The 60-mc proton (see Figure 21) and 46.4-mc fluorine (Figure 22) NMR spectra were obtained using a $DCDCl_3$ solution with TMS and $CFCl_3$ as internal references. The assignments are as follows:

H'. The quartet at 4.45 ppm and the triplet at 1.40 ppm are assigned to the carboethoxy ethyl groups.

F^{19}. The signal at -18.6 ppm is assigned to the fluorimino fluorine (syn- and anti- forms are no longer distinguishable for this group in difunctional compounds). The signal at +54.04 ppm (triplet, splitting 7.0 ± 0.5 cps) and the signal at +59.58 ppm (doublet of doublets, splittings 8.0 ± 0.2 and 12.1 ± 0.2 cps) are assigned to the syn-

and anti- -NFCO- fluorines. These splittings must result from coupling to the fluorimino fluorine and to the other -NFCO-. Thus, one splitting in one -NFCO- multiplet should correspond to one splitting in the other reflecting their mutual coupling. The agreement of the observed values (7.0 ± 0.5 cps versus 8.0 ± 0.2 cps) is rather poor.

The foreruns of DC_2PFG distillation were combined and the combined material was fractionated to give 1.2 g of 1-carboethoxyperfluoroguanidine (C_2PFG), identified by its infrared spectrum.

h. 1,3-Dicarboisopropoxyperfluoroguanidine ($DC_{3i}PFG$)

A solution of 23 g (0.1 mole) of 1,3-diisopropoxyguanidine in 350 ml of acetonitrile was fluorinated at 0 to -10°C until 0.3 moles of fluorine was consumed (1.0 hour). The fluorination mixture was worked up in an identical manner as given under g, to give 12 g (42% yield) of $DC_{3i}PFG$, bp 80°C/0.1-0.2 mm.

Anal. Calc'd for $C_9H_{14}N_3F_3O_4$: C, 37.90; H, 4.95; N, 14.73; F, 19.19.
Found: C, 37.9; H, 4.7; N, 15.0; F, 20.0.

The infrared spectrum of the compound is shown in Figure 20. Its impact sensitivity determination is not yet completed, but preliminary testing indicates that the compound is at least as sensitive to impact as DC_2PFG (see paragraph g).

The 60-mc proton (see Figure 23) and 56.4-mc fluorine (Figure 24) NMR spectra were obtained using a $CDCl_3$ solution with TMS and $CFCl_3$ added as internal references. The assignments are as follows:

H'. The 1.40 ppm doublet and 5.17 ppm septet are assigned to the isopropyl groups.

F^{19}. The -18.54 ppm signal is assigned to the fluorimino fluorine. The signal at +53.65 ppm (doublet of doublets, splittings 5.9 ± 0.3 cps and 7.9 ± 0.3 cps) and the signal at +60.25 ppm (doublet of doublets, splittings 8.8 ± 0.4 cps and 11.0 ± 0.2 cps) are assigned to syn- and anti- -NFCO-fluorines. As with DC_2PFG (see g), two of the multiplet splittings should coincide. The agreement is better in this case (7.0 ± 0.3 cps versus 8.8 ± 0.4 cps) although still not entirely satisfactory.

The proton and fluorine spectra are consistent with $DC_{3i}PFG$ structure.

Foreruns of $DC_{3i}PFG$ distillation were combined and the combined liquid fractionated to give 2.6 g of 1-carboisopropoxyperfluoroguanidine, $C_{3i}PFG$, identified by comparing its infrared spectrum with that of a known sample.

i. Attempted Nitration of $DC_{3i}PFG$

To 16 g of 100% nitric acid at -10°C was added dropwise with efficient stirring, 1.5 g of $DC_{3i}PFG$. No reaction was noticed and a clear solution resulted. The reaction mixture was allowed to warm up to 22-25°C at which temperature a slow gas evolution began. The reaction was mildly exothermic and external cooling was occasionally applied to keep the reaction temperature at 25°C. After 1.5 hours the gassing slowed down considerably and the reaction mixture was poured into 200 g of ice water. The resulting mixture containing ca. 0.3 ml of water-insoluble liquid was extracted with two 5-ml portions of carbon tetrachloride. The combined extracts were dried and filtered, and the solution was examined by infrared. Its infrared spectrum was identical with that of $DC_{3i}PFG$.

C. FLUORAMMONIUM SALTS (A. Remanick and V. Grakauskas)

1. Discussion

During this report period, emphasis was placed on establishing physical and chemical properties of fluorammonium perchlorate (SAP).

Storage stability tests, based on periodic fluorine analyses of SAP samples (summarized in Table 4, see Experimental), indicated that the material is stable in nickel containers, at room temperature for at least 3 months. In Monel, there appeared to be a small amount of decomposition within this period, whereas both stainless steel and Teflon were unsatisfactory.

Electrostatic sensitivity testing (in an argon atmosphere) showed a 50% firing level of 5 joules, compared to 8 joules for RDX. Because of the relative insensitivity of SAP, manipulations will be conducted without the use of remote-handling facilities. Scale-up of SAP is now in progress.

Some reactions of the fluorammonium cation were investigated using the more readily available fluorammonium methanesulfonate (SAM). The reaction of SAM with water appeared to be complex. About 50% of the original nitrogen was

liberated as the element. Both ammonia and hydrazine were found in the aqueous solution but nitrate ion, nitrite ion, and hydroxylamine were absent. Since ethyl N-fluorocarbamate reacts with aqueous base to yield ethyl N-hydroxycarbamate, it was expected that basic displacement on fluoramine leading to hydroxylamine might also occur. However, this reaction was not observed, and only inorganic salts were obtained when SAM was reacted with methanolic sodium methoxide. Only a very small amount of n-butylhydrazine was produced when SAM was reacted with n-butylamine.

The reaction of SAM with acetic anhydride gave N-methylacetamide, probably by the following mechanism:

$$FNH_3^+SO_3H + (CH_3CO)_2O \xrightarrow{CH_3CO_2H} \left[CH_3CONHF\right] \longrightarrow CH_3NCO + HF$$

$$CH_3NCO + CH_3CO_2H \longrightarrow CH_3NHCOOCCH_3 \longrightarrow CH_3CONHCH_3 + CO_2$$

SAM did not react with phthalic anhydride at room temperature.

2. Experimental

a. Storage Stability of SAP

Two batches of SAP purified by sublimation, and a third batch purified by column chromatography were each divided into several small containers of Teflon, nickel, stainless steel (321), and Monel. The loosely capped containers were then stored over P_2O_5 in separate glass jars. Periodic fluorine analyses of each sample are shown in Table 4.

b. Reaction of Fluorammonium Methanesulfonate with Water

In a 100-ml three-neck flask equipped with a magnetic stirrer, a pressure equalized dropping funnel, and a gas burrette, was placed 20 ml of water. A solution of 1.50 g (0.0115 mole) of SAM in 4 ml of methanesulfonic acid was placed in the dropping funnel. The system was flushed with helium and closed to the atmosphere. The SAM solution was added dropwise to the water over a 2-hour period. Nitrogen evolved during this time and 54.4 ml of the gas (STP) was collected in the gas burrette. Gas chromatographic analysis showed only nitrogen. The residual aqueous solution was diluted to 100 ml and aliquots were withdrawn for analysis. The solution contained 0.063 mg/ml hydrazine and

0.24 mg/ml ammonia. Tests for nitrate, nitrite, and hydroxylamine were negative. Dumas nitrogen showed 0.62 mg/ml.

c. Reaction of Fluorammonium Methanesulfonate with n-Butylamine

To a solution of 2.3 g (0.017 mole) of SAM in 40 ml of ether at -80°C was added 10.0 g (0.125 mole) of n-butylamine in 30 ml of ether. The solution was stirred, allowed to warm to room temperature, and refluxed for 30 min. The reaction mixture was filtered and the filtrate concentrated to remove the solvent and unreacted n-butylamine. The residual liquid was distilled to give a few drops of n-butylhydrazine, identified as its oxalate salt, mp 162-3°C (reported* mp 165°C).

Anal. Calc'd for $C_6H_{14}N_2O_4$: C, 40.4; H, 7.86.
Found: C, 40.3; H, 7.94.

d. Reaction of Fluorammonium Methanesulfonate with Acetic Anhydride

To 2.62 g (0.020 mole) of SAM in 10 ml of acetic acid was added 2.2 ml (ca. 2.38 g; 0.024 mole) of acetic anhydride. The mixture was stirred for 2.5 hours and 1.0 ml of acetic anhydride was added. After 30 min, the solution became homogeneous. Gas slowly evolved from the reaction mixture during the entire 3-hour period. The solution was poured into 75 ml of ether and the mixture was neutralized with solid sodium carbonate. The solution was filtered and concentrated at reduced pressure. Distillation of the residue at 80°C/10 mm yielded 0.4 g of liquid, which solidified in the receiver. The IR spectrum of the solid was idertical to that of an authentic N-methylacetamide.

III. PERSONNEL

The experimental work was performed by K. Baum, V. Grakauskas, M. P. Mascari, A. Quan, A. H. Remanick, and O. S. Schaeffler. Analytical support was provided by C. L. Deuel (gas chromatograph), K. Inouye (microanalyses), and H. M. Nelson (IR and NMR).

*G. Gever and K. Hayes, J. Org. Chem., 14, 813 (1949).

TABLE 1

1-CARBOALKOXYGUANIDINES, $NH_2C(=NH)NHCO_2R$

R	mp °C	Yield, %	Analyses, % Calc'd C	Calc'd H	Calc'd N	Found C	Found H	Found N
CH_3	163-5	60	28.6	6.4	33.2	28.4	6.2	32.8
C_2H_5 **	100-102	40						
i-C_3H_7	143-5	55	41.4	7.6	29.0	41.5	7.7	28.3
n-C_4H_9		70	45.3	8.2	26.4	45.4	8.1	26.7

*Hemihydrate.
**Literature mp for hemihydrate is 100°C.

TABLE 2

1,3-DICARBOALKOXYGUANIDINES, $NH=C(NHCO_2R)_2$

R	mp °C	Yield, %	Analyses, % Calc'd C	Calc'd H	Calc'd N	Found C	Found H	Found N
C_2H_5	160-1*	45						
i-C_3H_7	170	40	46.74	7.41	18.17	46.6	7.5	18.2
n-C_4H_9	122	35	50.95	8.12	16.21	50.9	8.2	16.2

*Reported mp 161-2°C.

TABLE 3

1-CARBOALKOXYPERFLUOROGUANIDINES, $NF_2C(=NF)NFCO_2R$

R	Analyses, % Calc'd C	Calc'd H	Calc'd N	Calc'd F	Found C	Found H	Found N	Found F
C_2H_5	23.65	2.50	20.69	37.41	24.4	2.86	21.1	35.9
i-C_3H_7	27.66	3.24	19.35	35.00	27.4	3.1	19.1	35.0
n-C_4H_9	31.17	3.93	18.18	32.88	31.2	4.1	17.8	31.2

TABLE 4

STORAGE STABILITY OF SAP

Container	Sample	Initial % F	% F After X Day Storage					
			7	14	30	60	90	150
Nickel	1-a	13.4	13.3	13.1	13.3			
	3-a	13.4				13.2		11.9
	2-a	13.1	13.2	13.0	13.2			
	4-a	13.1				14.1		
	5-b	13.2	13.0	13.1	13.0		10.5	
	7-b	13.2					13.2	
Monel	1-a	13.4	12.2	13.0	12.8	12.9		10.9
	3-a	13.4						11.9
	2-a	13.1	12.8	13.2	12.9		8.4	
	4-a	13.1					12.8	
	5-b	13.2	13.1	13.0	12.3		14.2	
	7-b	13.2						
Stainless Steel 321	1-a	13.4	dec					
	3-a	13.4	12.1	12.2	12.5	11.7		
	2-a	13.1	12.3	12.3	12.5		12.6	
	4-a	13.1					13.0	
	5-b	13.2	12.4	12.4	12.2		10.9	
	7-b	13.2					9.9	
Teflon	1-a	13.4	12.0	dec				
	3-a	13.4		dec				
	2-a	13.1	13.1	12.0	10.3		dec	
	4-a	13.1					dec	
	5-b	13.2	12.8	13.1	dec			
	7-b	13.2			12.0		dec	

a - purified by sublimation.

b - purified by chromatography.

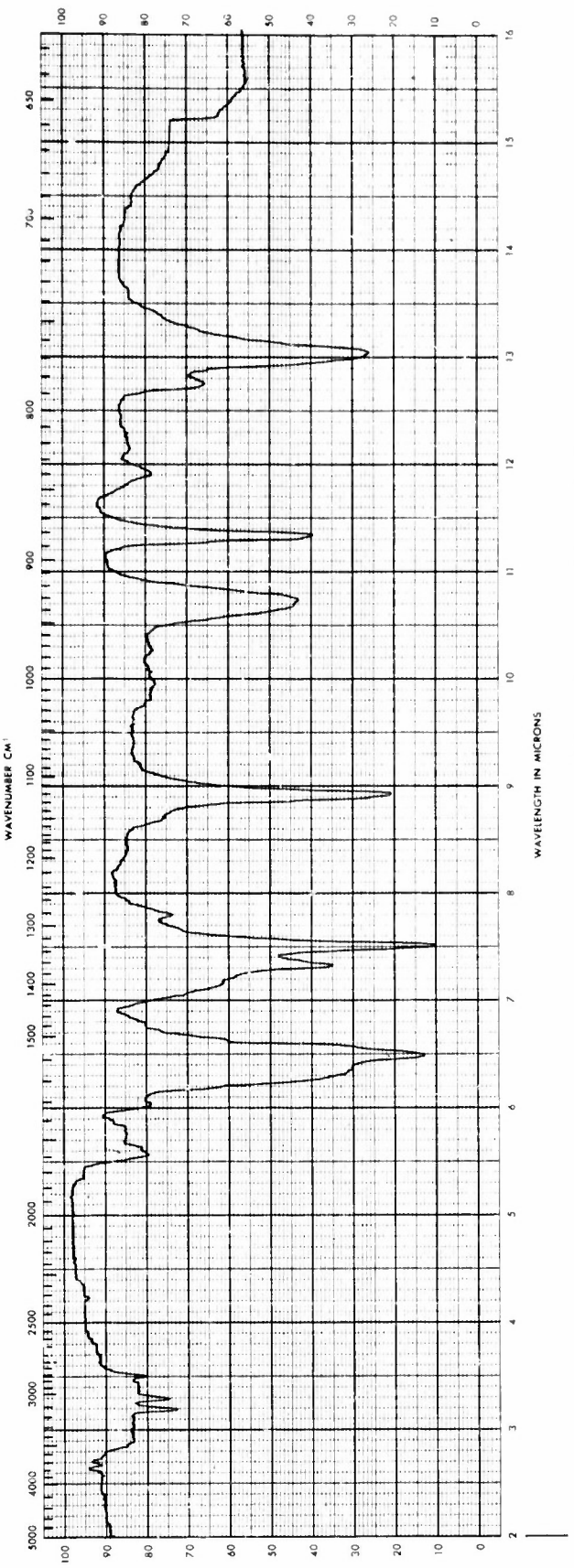

Fig. 1. Infrared Spectrum of 1-Chloro-1-nitroethylene

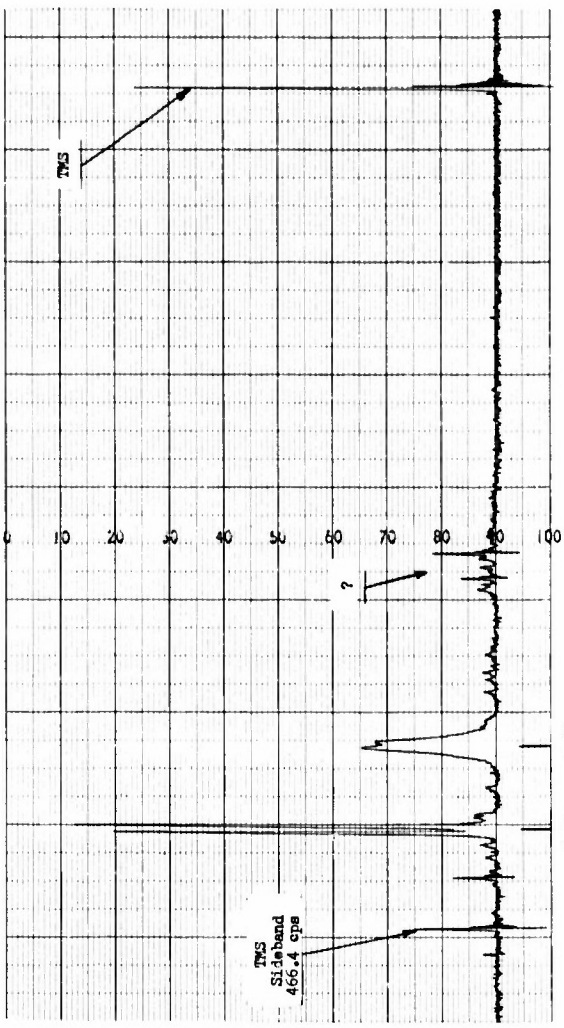

Fig. 2. Proton NMR Spectrum of 1-Chloro-1-nitroethylene

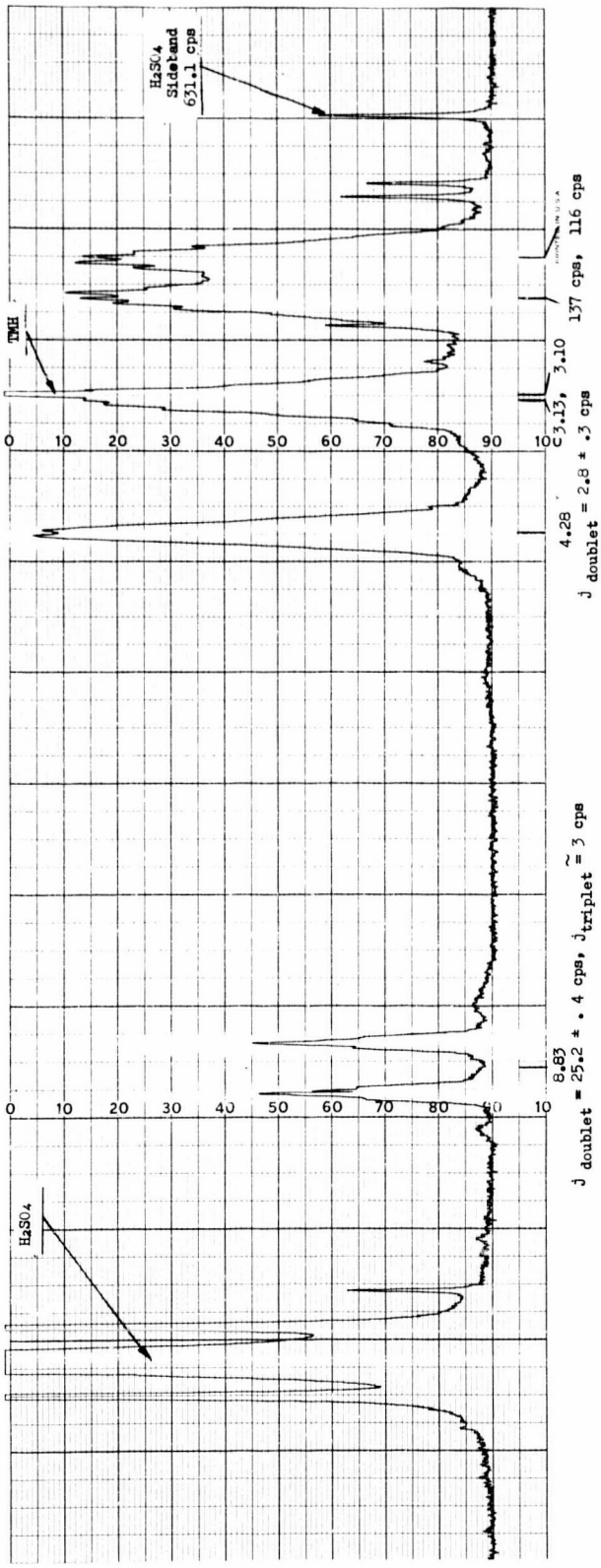

Fig. 3. Proton NMR Spectrum of Cyclopentyldifluoramine-Sulfuric Acid Reaction Product

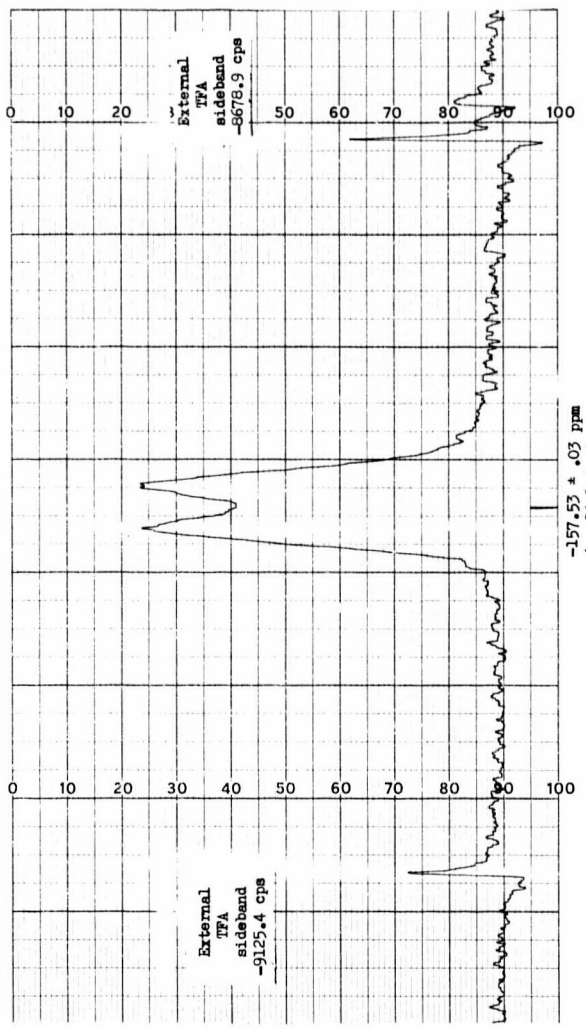

Fig. 4. Fluorine NMR Spectrum of Cyclopentyldifluoramine-Sulfuric Acid Reaction Product

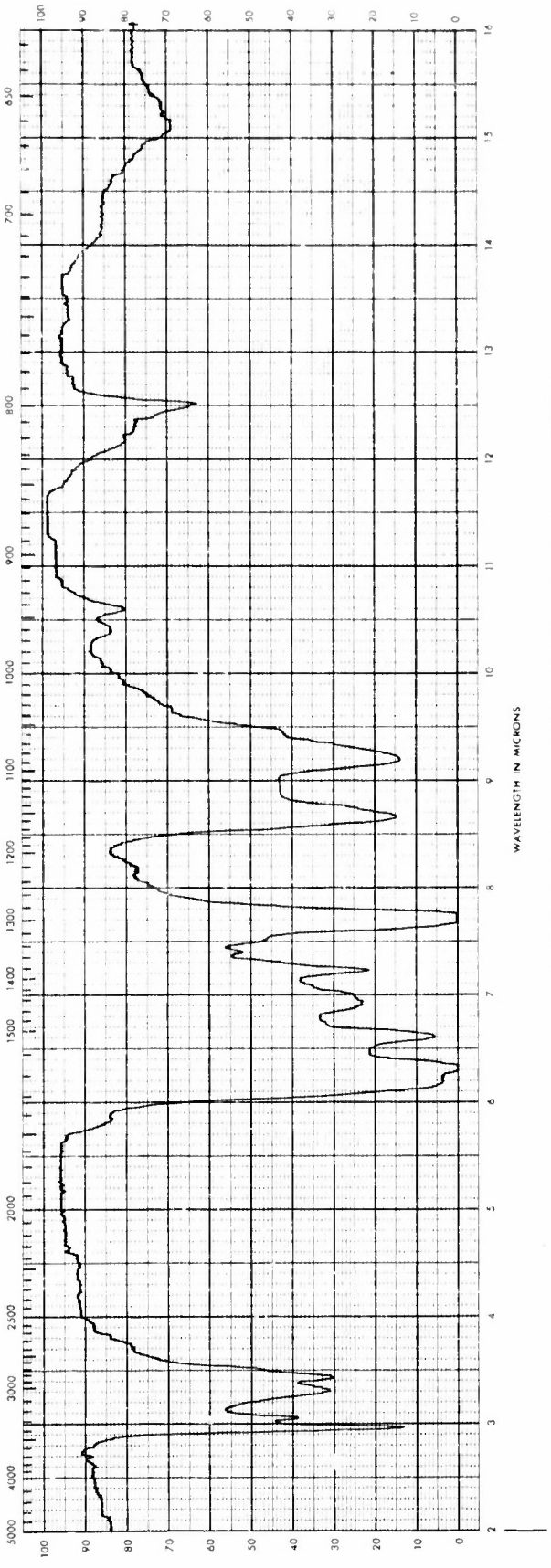

Fig. 5. Infrared Spectrum of 1-Carbo-n-butoxyguanidine

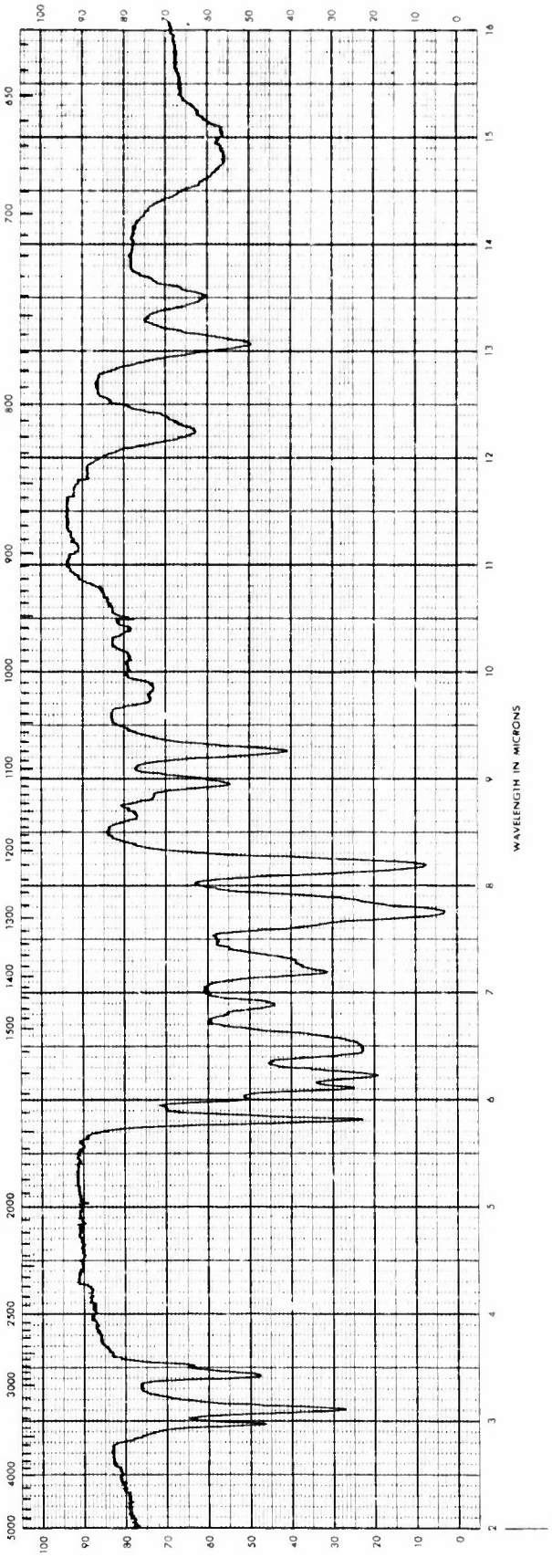

Fig. 6. Infrared Spectrum of 1,3-Dicarbo-n-butoxyguanidine

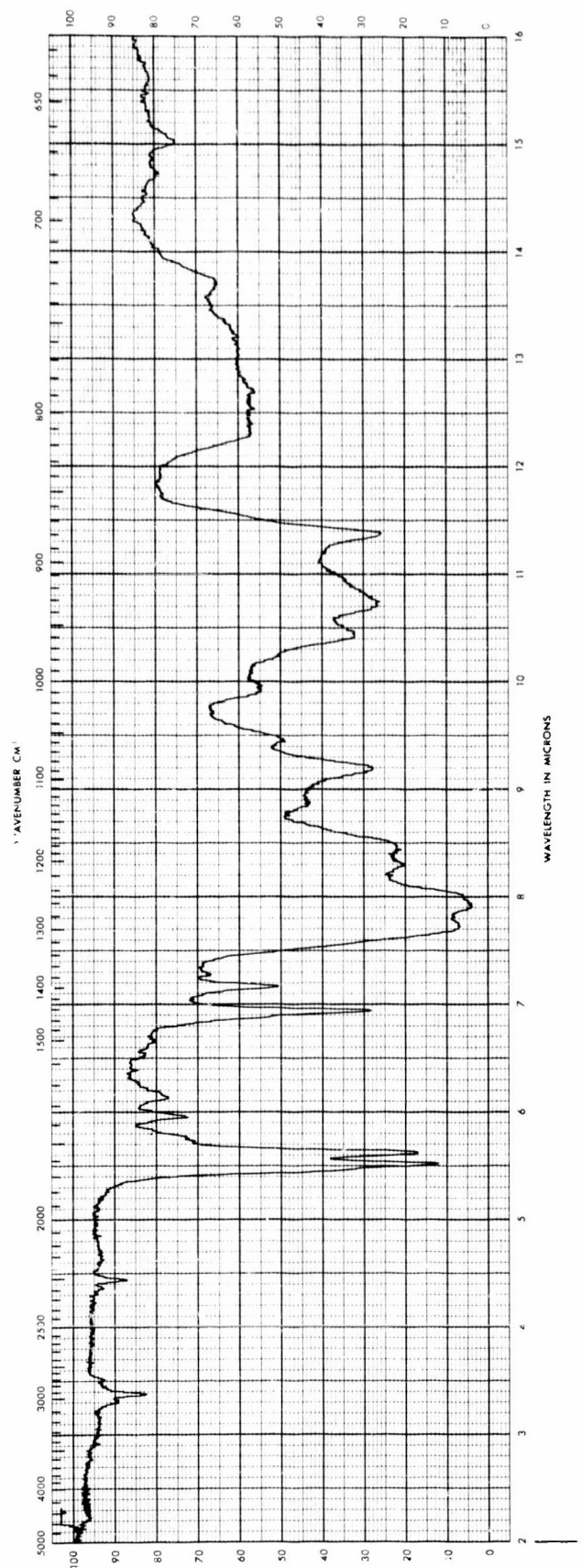

Fig. 7. Infrared Spectrum of 1-Carbomethoxyperfluoroguanidine (C_1PFC)

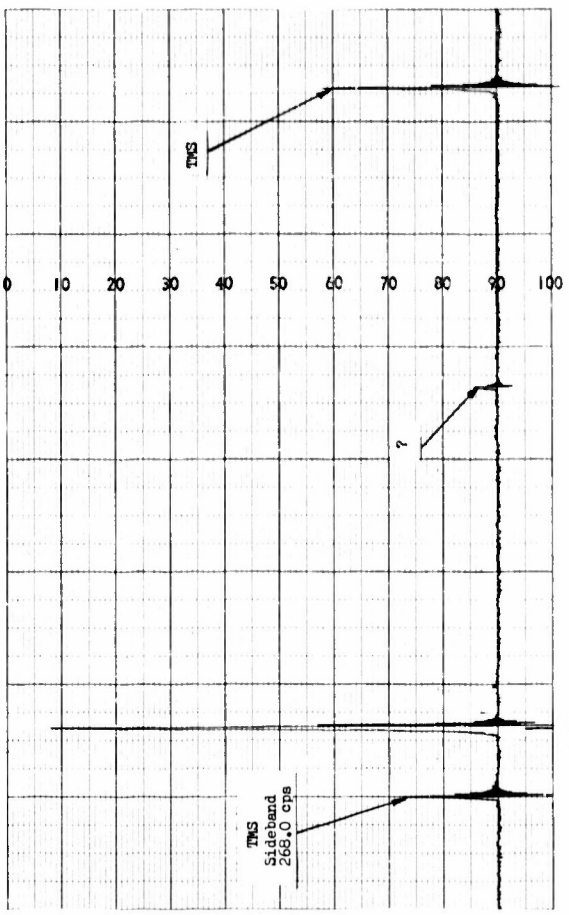

Fig. 8. Proton NMR Spectrum of 1-Carbomethoxyperfluoroguaridine (C_1PFG)

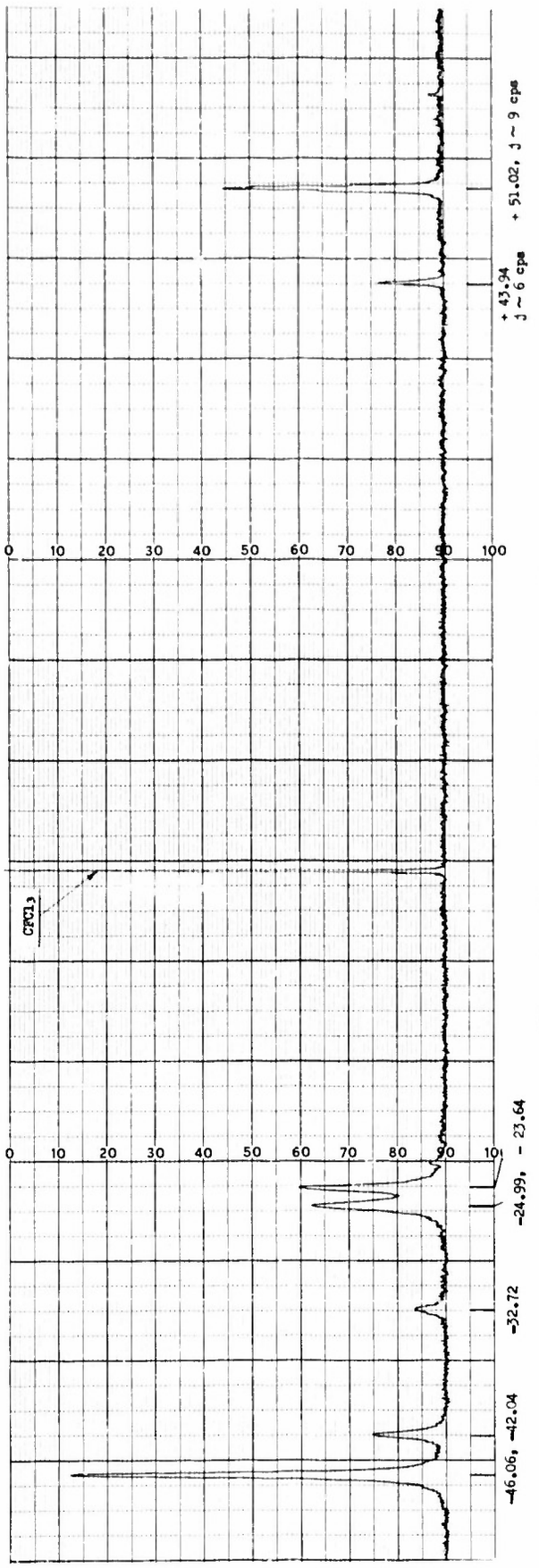

Fig. 9. Fluorine NMR Spectrum of 1-Carbomethoxyperfluoroguanidine (C_1PFG)

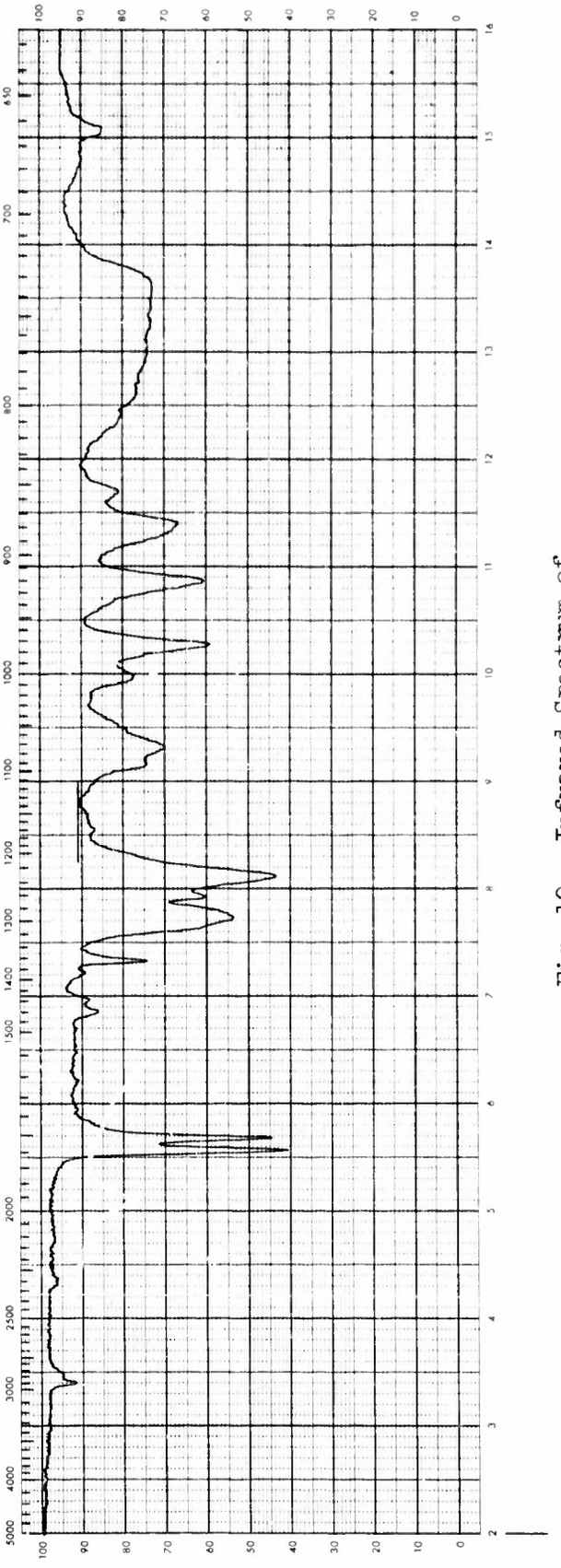

Fig. 10. Infrared Spectrum of 1-Carboethoxyperfluoroguanidine (C_2PFG)

Figures 9 and 10

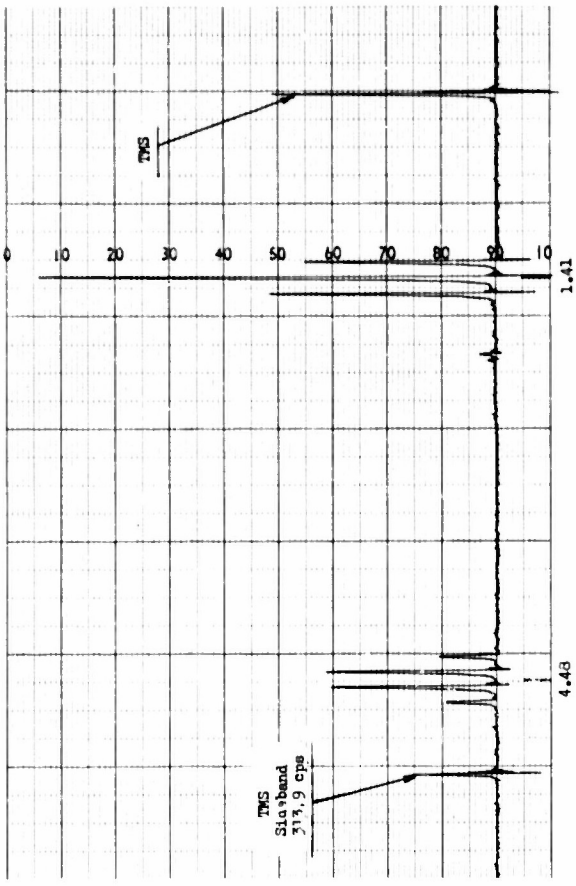

Fig. 11. Proton NMR Spectrum of 1-Carboethoxyperfluoroguanidine (C_2PFG)

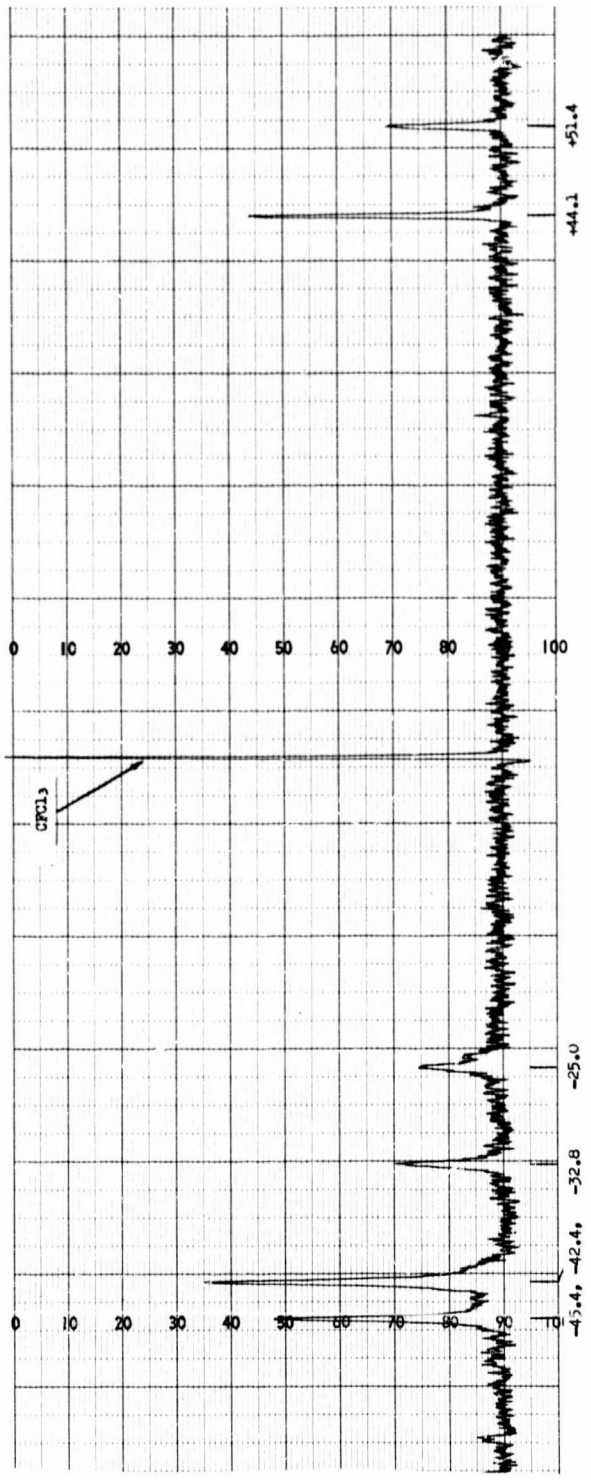

Fig. 12. Fluorine NMR Spectrum of 1-Carboethoxyperfluoroguanidine (C_2PFG)

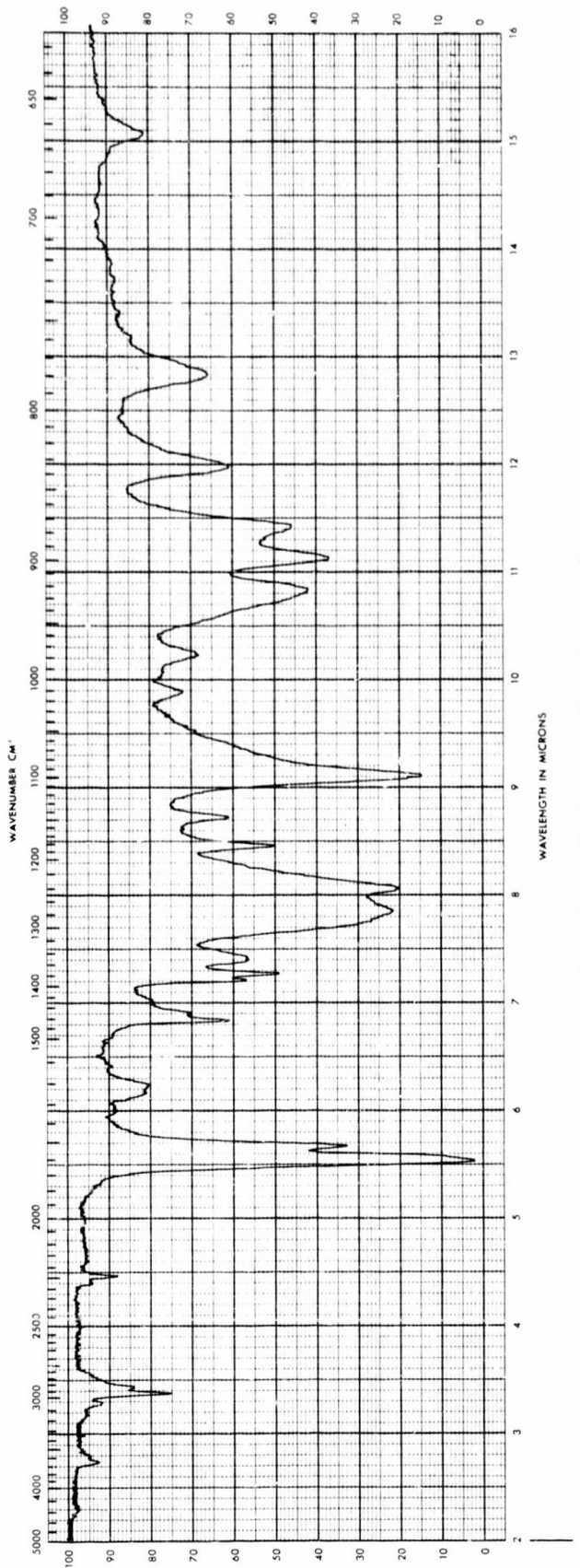

Fig. 13. Infrared Spectrum of 1-Carboisopropoxyperfluoroguanidine (C_{3i}PFG)

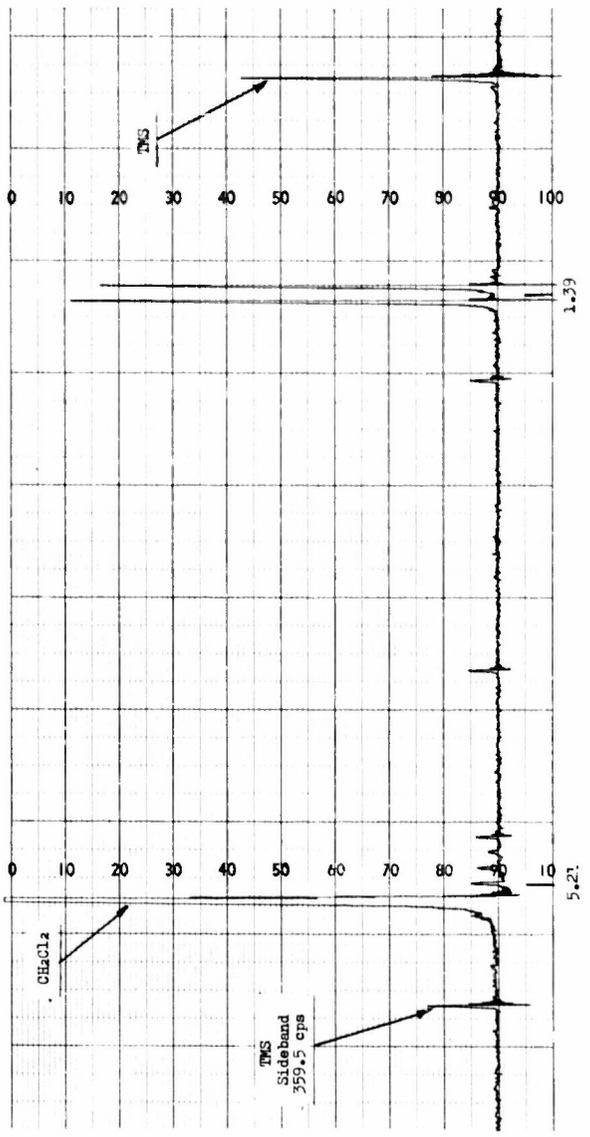

Fig. 14. Proton NMR Spectrum of 1-Carboisopropoxyperfluoroguanidine (C_{3i}PFG)

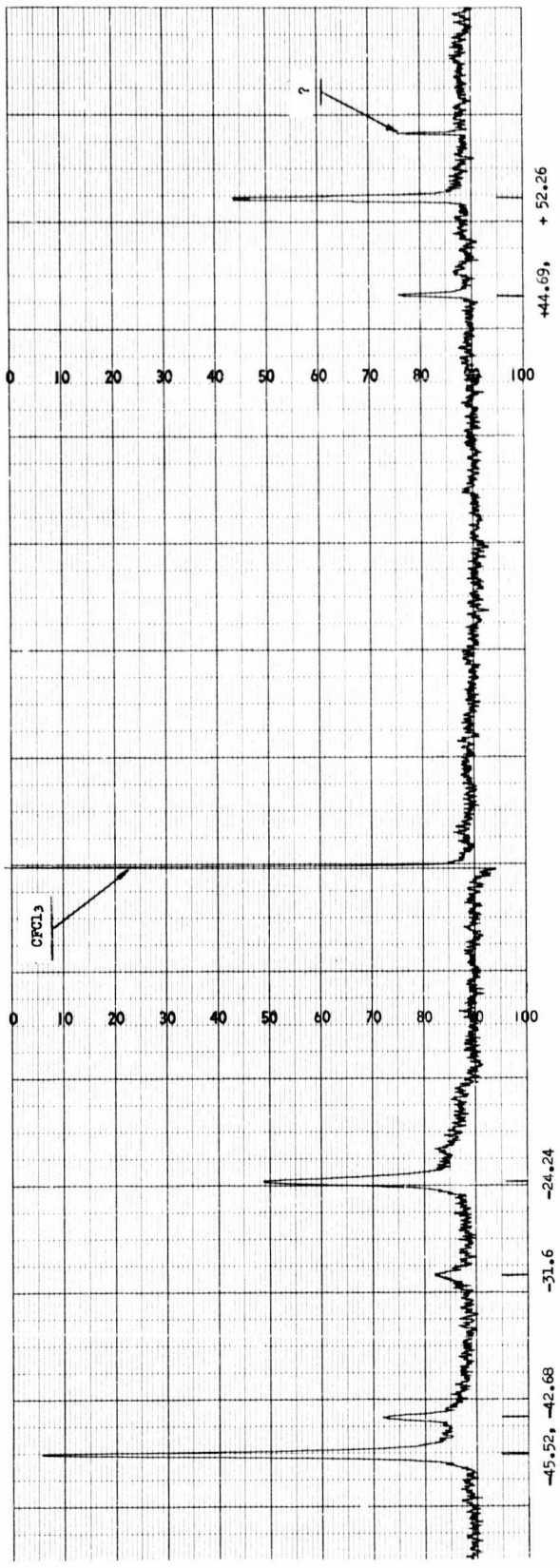

Fig. 15. Fluorine NMR Spectrum of 1-Carboisopropoxyperfluoroguanidine (C_{3i}PFG)

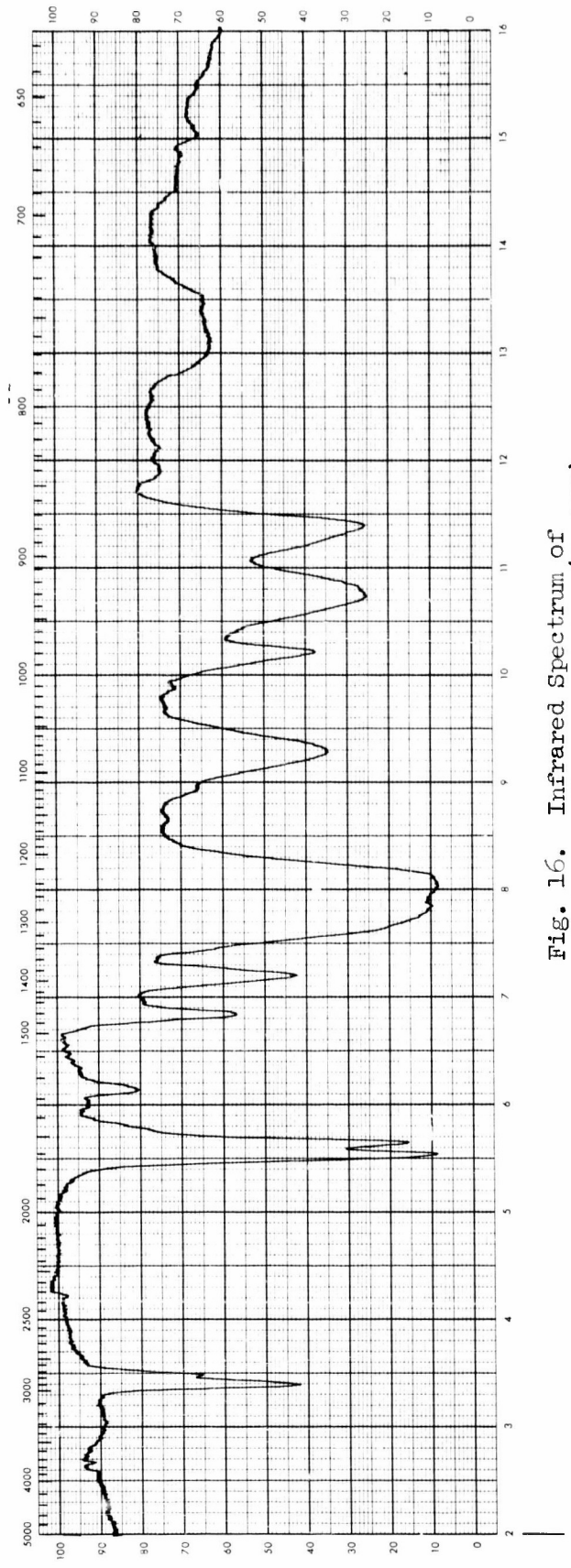

Fig. 16. Infrared Spectrum of 1-Carbo-n-butoxyperfluoroguanidine (C_{4n}PFG)

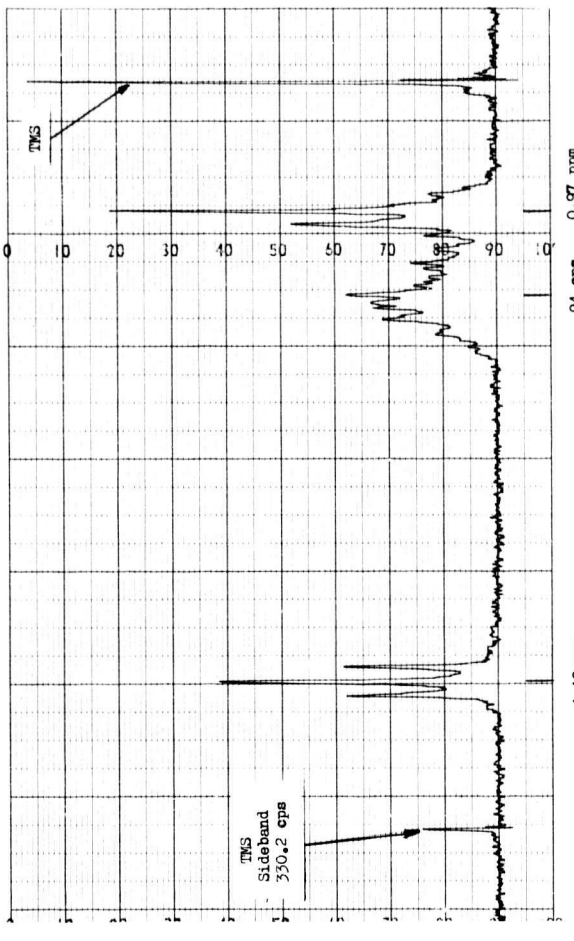

Fig. 17. Proton NMR Spectrum of 1-Carbo-n-butoxyperfluoroguanidine (C_{4n}PFG)

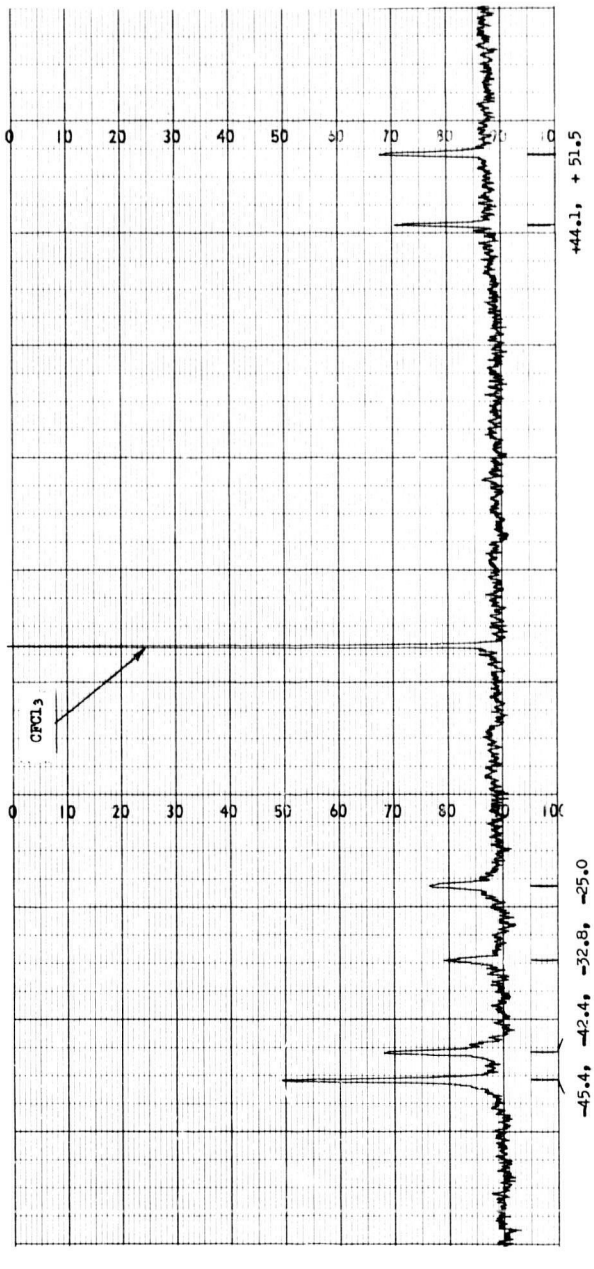

Fig. 18. Fluorine NMR Spectrum of 1-Carbo-n-butoxyperfluoroguanidine (C_{4n}PFG)

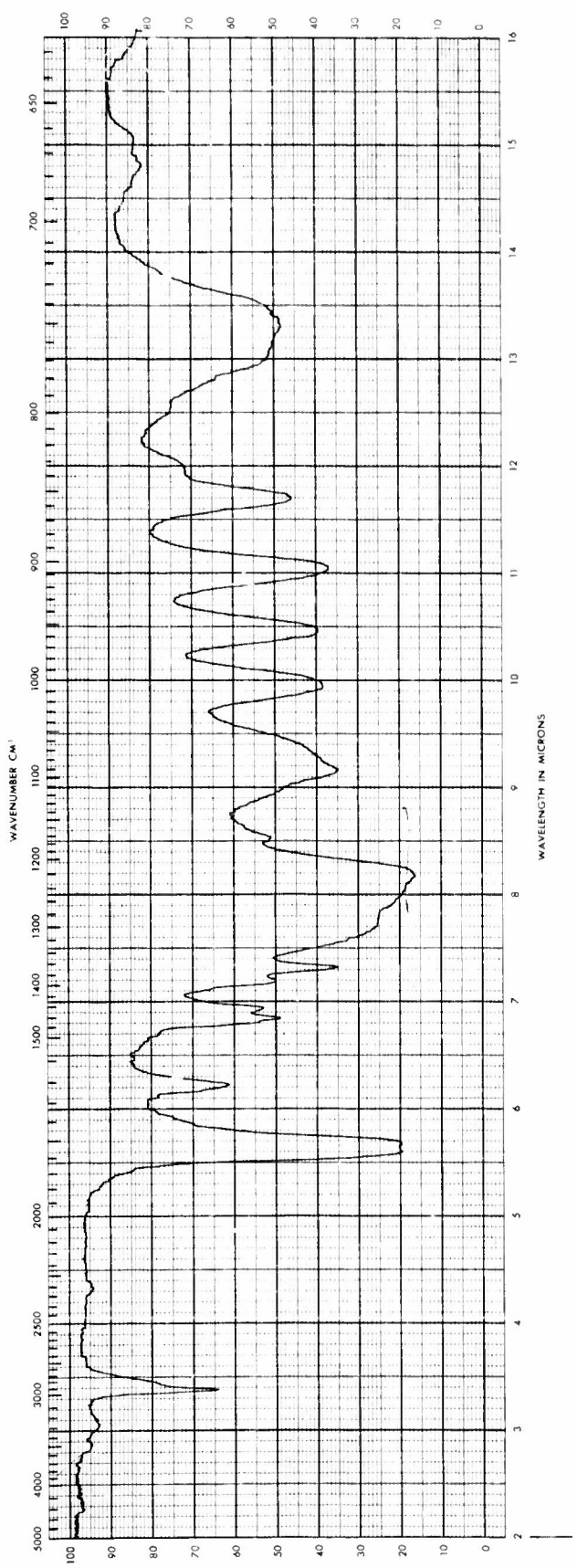

Fig. 19. Infrared Spectrum of 1,3-Dicarboethoxyperfluoroguanidine (DC_2PFG)

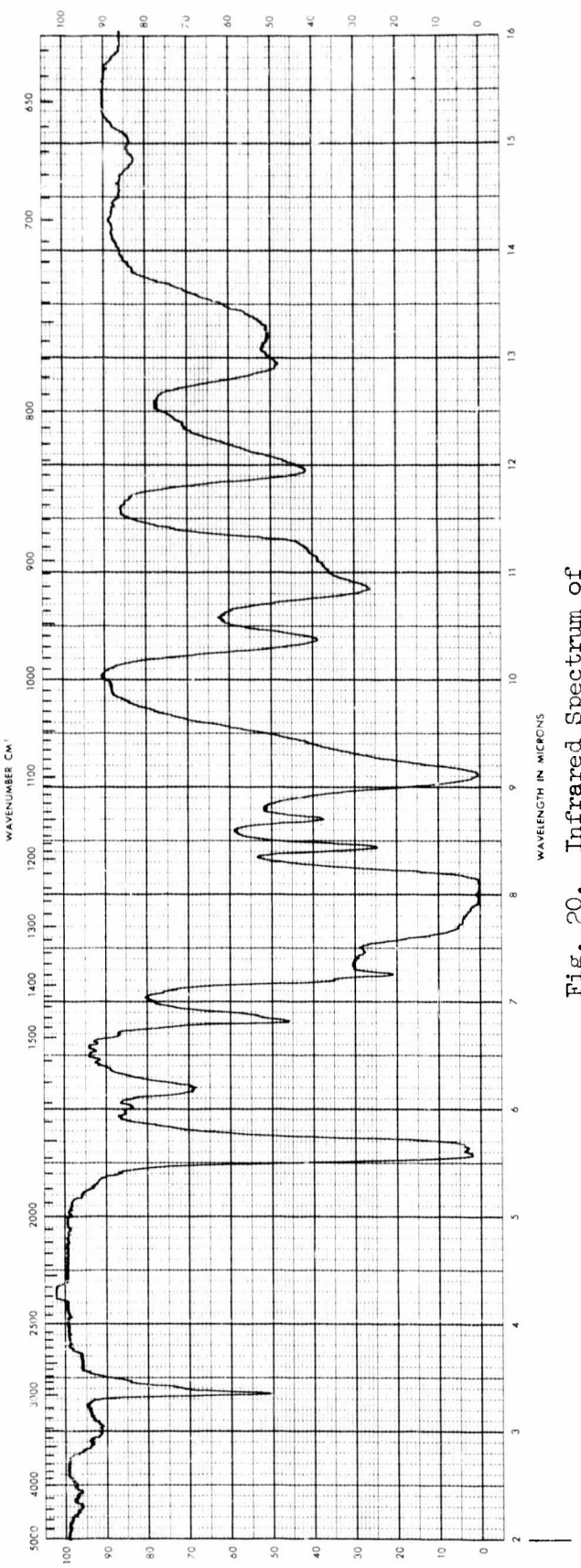

Fig. 20. Infrared Spectrum of 1,3-Dicarboisopropoxyperfluoroguanidine ($DC_{3i}PFG$)

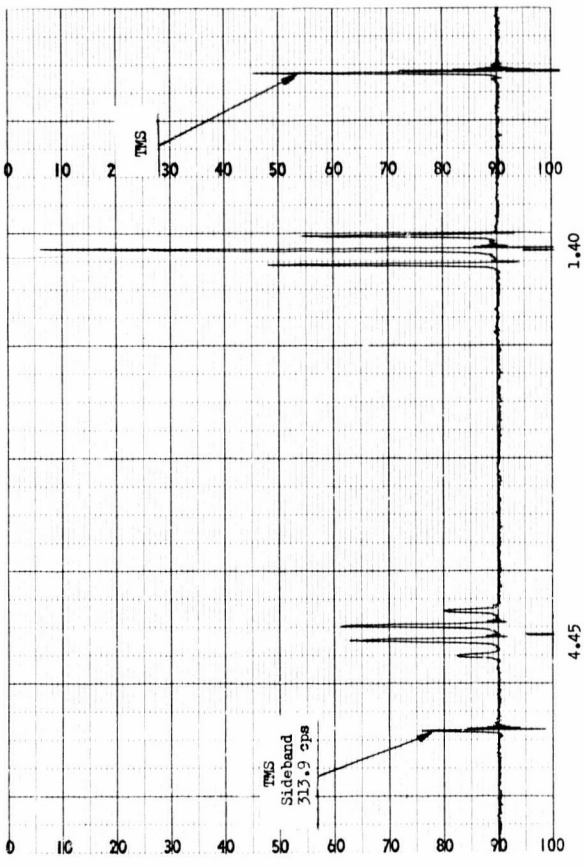

Fig. 21. Proton NMR Spectrum of 1,3-Dicarboethoxyperfluoroguanidine (DC_2PFG)

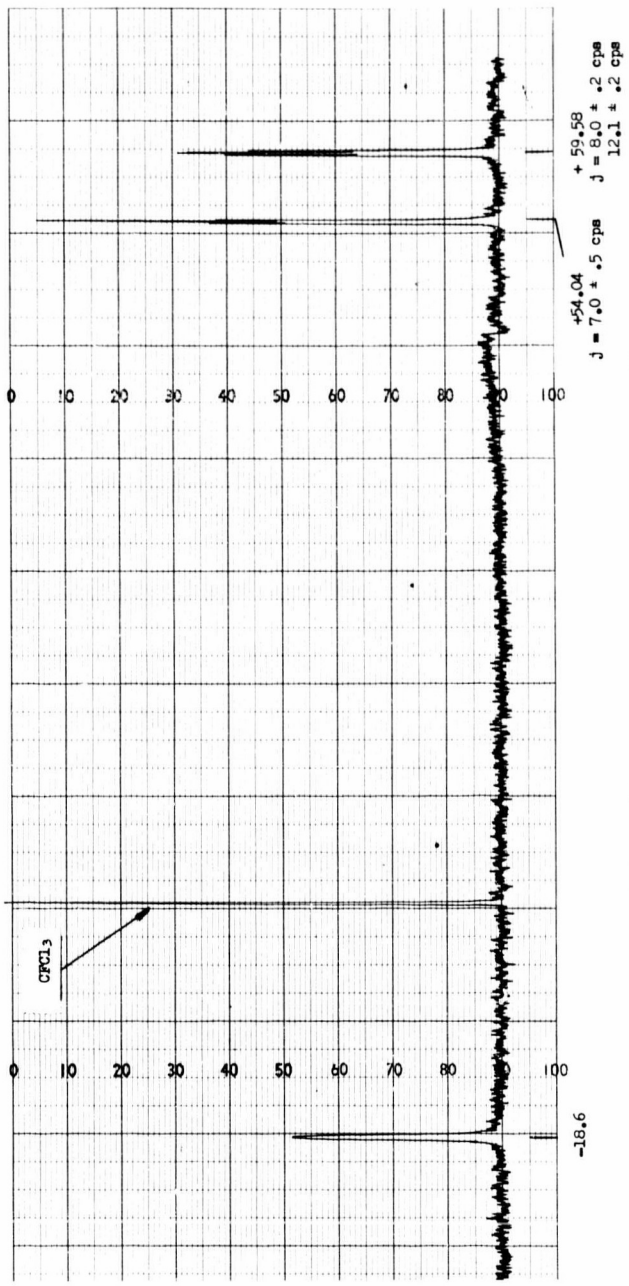

Fig. 22. Fluorine NMR Spectrum of 1,3-Dicarboethoxyperfluoroguanidine (DC_2PFG)

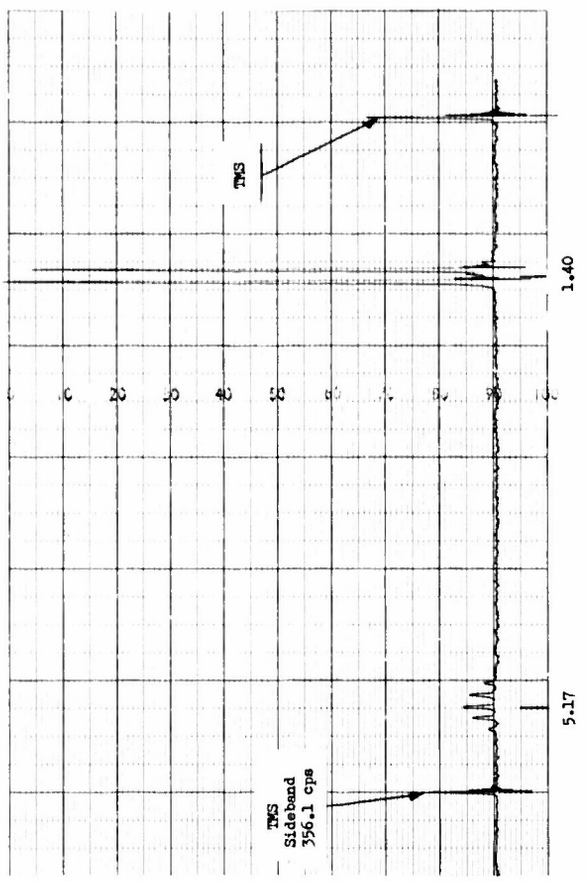

Fig. 23. Proton NMR Spectrum of 1,3-Dicarboisopropoxyperfluoroguanidine ($DC_{3i}PFG$)

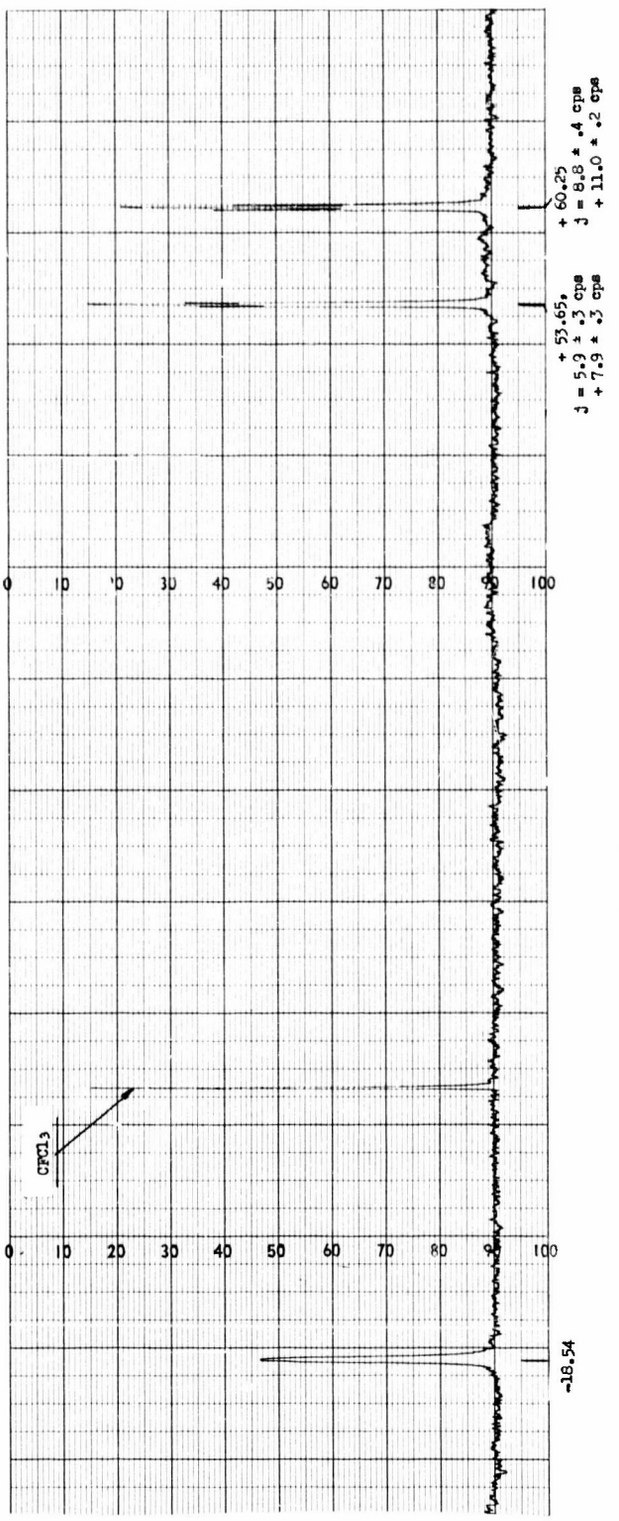

Fig. 24. Fluorine NMR Spectrum of 1,3-Dicarboisopropoxyperfluoroguanidine ($DC_{3i}PFG$)

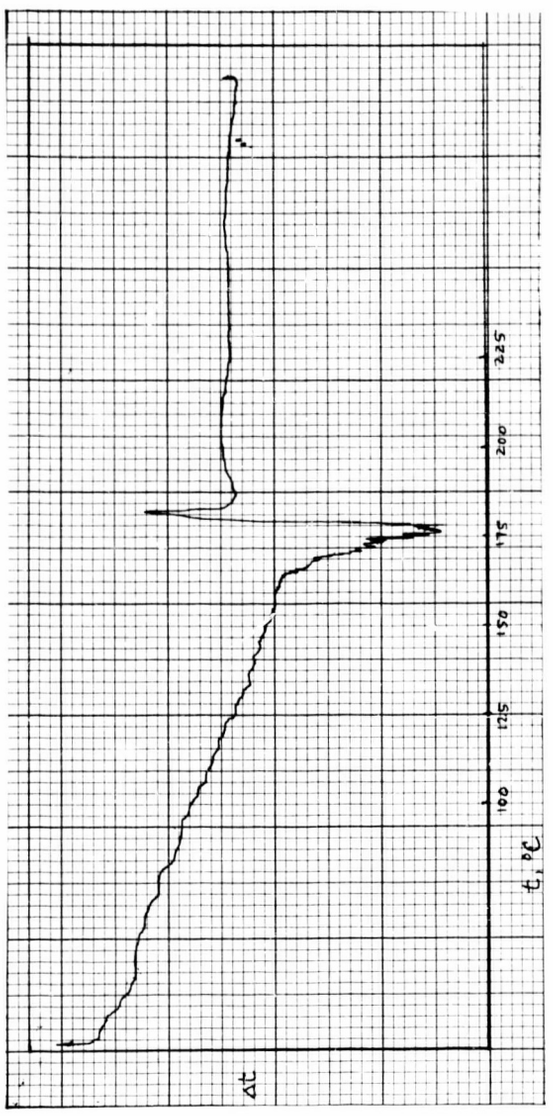

Fig. 25. Differential Thermal Analysis of 1-Carbo-n-butoxyperfluoroguanidine (C_{4n}PFG)

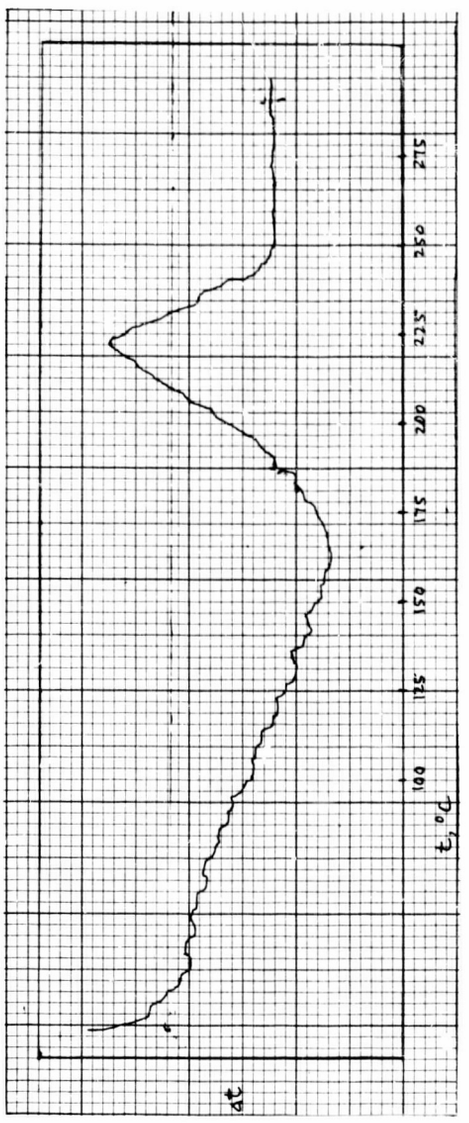

Fig. 26. Differential Thermal Analysis of 1-3-Dicarboisopropoxyperfluoroguanidine (DC_{31}PFG)